Particulate Matter Inhalled Per Day by an Average Individual

I. Reference Air Pollution Handbook (p. 2-43)

Concentration of Suspended Particulate Matter in the Atmosphere of a Number of Communities

	Minimum	Maximum	Mean
	Micrograms/Liter of Air		
Baltimore - Downtown	0.21	1.72	0.87
- Industrial	0.05	1.46	0.38
Cincinnati - Industrial	0.01	1.98	0.42
- Residential	0.01	1.30	0.28
Donara, Pa.	0.00	2.50	0.74
Los Angeles, Detroit San Francisco, Washington	0.25	0.47	0.51

II. J. E. Hardcastle's report of April 14, 1958

Particulate matter inhaled by an average individual is based on the following:

$$\text{Volume of air taken in per day} = \frac{(15 \text{ breathes})}{\text{min.}} \frac{(60 \text{ min.})}{\text{hr.}} \frac{(24 \text{ hrs.})}{\text{day}} \frac{(0.8 \text{ liter})}{\text{breath}} = 17280 \text{ liters/day}$$

Amount of suspended particulate matter inhaled per day

	Micrograms/day		
	Minimum	Maximum	Mean
Baltimore - Downtown	363.0	2975	1508
- Industrial	86.5	2520	657
Cincinnati - Industrial	17.3	3520	727
- Residential	17.3	2250	484
Donara, Pa.	0.0	4320	1280
Los Angeles, Detroit San Francisco, Washington	432.0	81.3	882

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THE SCIENTIFIC ASPECTS OF BENTONITE

In commencing a study of bentonites, as well as other clays, we need to picture the fundamental clay minerals because their pattern influences clay behavior fully as much as the chemical elements of which they are composed.

THE CLAY MINERALS

Pure clay is a mass of mineral fragments, strongly bound together when dry, but separable—when dispersed in water—into myriads of particles so small that many of them are beyond microscopic visibility.

To understand the variable activities of clays, we must start with the invisible world of atoms and molecules and form a mental picture of the way they are assembled to form clay substance. Atoms of silicon, aluminum, and oxygen,* with hydrogen atoms clinging to them, are united in symmetrical patterns to form a molecule; clusters of molecules interlock to form "flake units"; aggregates of flake units form the tiniest particles of what we call clay substance. Literally millions of flake units are needed to make a particle large enough to be visible to the human eye.

Practically the same "materials of construction" form the basis for all clay flakes regardless of the type of clay but the architectural patterns in which these materials are joined are not the same. The difference in pattern is an underlying reason for vividly different properties of the clay itself.

The dissimilar assembly of the atoms permits distinct identification by X-ray methods. Fortunately there are only a few common patterns and they are given different "clay mineral" names. The three principal ones are:

Montmorillonite—the chief clay mineral of bentonite.

Kaolinite—the main constituent of fire clays, china clays, kaolins and ball clays.

Illite—largely found in shales.

There are other clay minerals of minor importance but we will discuss only the first two since they form the basis for most of the commercially useful clays, and for simplicity we will designate montmorillonite as "M" and kaolinite as "K".

*Chiefly those but not exclusively. Magnesium, potassium and iron sometimes occupy positions in the molecule, replacing aluminum.

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Molecular Structure

All clays are described as "silicates of alumina" because silicon and aluminum are the primary elements of clay composition. These elemental atoms are assembled in distinct layers of two kinds—silicon-oxygen sheets and aluminum-oxygen sheets. The sheets are combined to form molecules and at this point we observe a radical difference. The M molecule has two silicon sheets with an aluminum sheet sandwiched between them, but the K molecule has only one silicon and one aluminum sheet. M is described as "Si-Al-Si" structure and K as "Si-Al" structure. Certain highly significant effects result from these structural differences.

Groups of molecules are inseparably joined in thin platey particles of definite thickness, but indefinite width and breadth. These are the flake units. The atomic bonds which hold the plate structure together are much stronger laterally than vertically. Laterally, the plates extend until they reach broken edges; vertically they extend only one molecule in thickness. The tops and bottoms of the plates are the basal planes and the thickness is scientifically referred to as the "c-dimension."

Let us conceive a multitude of dry flake units massed together to form a particle of clay substance. Because of their flat shape their plane surfaces are approximately parallel—somewhat like a deck of playing cards flung onto a table. When wetted, they cleave apart, and while not every flake splits away from its neighbors, a large proportion of the M flakes and a less proportion of the K flakes do become individually dispersed.

The cleavage occurs mainly along the basal planes, and therein lies the reason for the greater dispersibility of M. With the Si-Al-Si structure, an Si sheet always faces an Si sheet of the next M flakes above and below it. Like mineral atoms have like electro-chemical charges; consequently the adjacent Si sheets do not attract but may even repel each other. On the other hand a pack of K flakes has Si sheets facing Al sheets of its neighbors, exercising, if anything, an attractive force which resists separation.

Hydration of the Lattice

A layer of water molecules coats the basal

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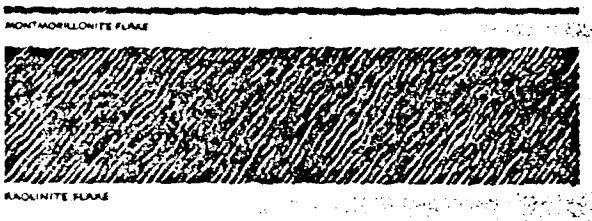
planes of the M flake units, tightly held by a mysterious force. A packet of super-imposed flakes has this layer of water molecules between the flakes even when air-dried; the packet forms what is called a "lattice" structure. When the lattice is wetted more water molecules crowd between the individual flakes, forming layer upon layer in semi-rigid positions, pushing the flakes apart and causing the mass to swell. When the water is removed the mass contracts and the flakes reassume approximately their original spacing.* The movement is only in one dimension, like that of an accordion. It may be repeated indefinitely and is more than simply a curious phenomenon since it leads to correlated activities that become signally valuable in industrial uses.

K flakes on the other hand do not attract layers of water molecules between their basal planes; consequently their spacing is fixed and the mass is not expandible. It requires extremely vigorous mechanical action in water to disperse K into nearly individual flakes. One investigator, using the electron-microscope has estimated the ratios of depth to breadth of clay mineral flake units. His findings indicated a ratio from 1/100 to 1/300 for M and from 1/5 to 1/25 for K. Thus the M flake units have tremendously greater surface area than those of K. The highly magnified colloidal activities of M result from its immense surface area relative to mass.

*A recently discovered process makes it possible to remove the water from swelled bentonite without causing contraction.



Relative Thickness of Flakes of M and K in Water Suspension

The performance of clays is profoundly affected by the kind and number of ions which cluster on the surface of the flakes and in the inter-planar surfaces. Montmorillonite is far more densely populated with attached ions than kaolinite and hence shows greater "ion activity" in water. Ion activity is discussed in a later chapter.

THE CLAY WATER SYSTEM

Clay becomes energized only when wetted. Physicists have formed a hypothetical picture of hydrated clay, being that of a core composed of a flake unit of the clay-mineral surrounded by a hull of water tightly bound to it by electro-static forces. Attached to the clay flake but not an integral part of its crystal structure are swarms of "ions", i.e. electrically charged atoms of other substances which are held by electro-static attraction.

The clay flake with its surrounding atmosphere of attached water molecules and ions is termed by physicists "the micelle." When suspended in a body of water the micelle moves about carrying its inseparable atmosphere with it, somewhat like a solar body in space.

The clay crystal, being composed mainly of aluminum, silicon and oxygen, is slightly acidic in character. The net balance of its electric charges is negative and therefore when suspended in water in an electric field the particles migrate to the anode or positive pole.

That is the broad picture of the water system of most clays, but certain of the effects are intensified when the clay-mineral is montmorillonite and particularly when it is sodium bentonite, to which this discussion will be confined, with Volclay as the prototype.

Hydration

A particle of Volclay bentonite substance is composed of flakes stacked one over the other, their flat sides together, but between each basal plane is a single layer of tightly held water molecules which exists even in air-dried samples. When the particle is wetted, more water molecules press between the flakes forming layer after layer. The distance between the flakes increases until the attractive force of the particle is no longer capable of adding to the thickness of the captive water hull.* Free water then flows between

*The water hull around saturated Volclay particles is so tightly held that it cannot be removed by pressures up to hundreds of pounds per square inch.

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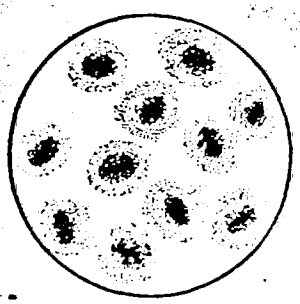
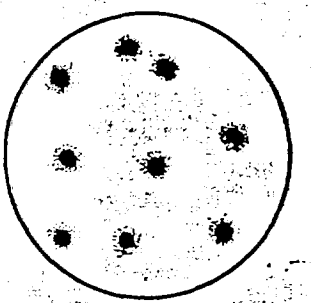
Source: https://www.industrydocuments.ucsf.edu/docs/jjmx0000

the semi-rigid water sheaths and the individual micelles float about in the liquid, each retaining its own overcoat of bound water. The micelles do not coalesce as long as the flake retains its electro-chemical charges because all are negative and the flakes mutually repel each other. This is a "disperse system" or sol, and the bentonite particles are "suspensoids".



Montmorillonite flakes (black) with attached water molecules (grey) leaving less "free" water for circulation.



Kaolinite flakes (black) with a smaller hull of water molecules (grey). Ample "free" water, hence no friction to create "viscosity."

When the concentration is sufficiently dilute to allow them "elbow room" the flakes are in almost constant motion, darting about in haphazard zig-zag fashion. This is a characteristic of colloidal sols known as the Brownian Movement and is explained by the kinetic theory of matter which postulates that all molecules are in motion. However, when the sol is allowed to stand quiescent, "gelation" ensues, Brownian Motion decreases and the flakes are held in fixed positions by counteracting electrical forces of attraction and repulsion. In moderately heavy concentrations the mass sets to a semi-solid of jelly-like consistency. Restirring or shaking immediately destroys the jelly-like formation and the sol reverts to its initial mobility, this reversible phenomenon being termed thixotropy. In some industrial uses of bentonite thixotropy is desirable, but often it is disadvantageous.

Electro-Chemical Forces

Montmorillonite molecules do not exist in the simple form of aluminum, silicon and water only; instead, some of the aluminum is replaced by magnesium, ferric and ferrous iron and possibly minor amounts of other ions, these substitutions being part of the fixed crystal structure of the mineral. Aluminum being tri-valent (having three ionic charges) while magnesium and ferrous iron have only two, there is created a valence deficiency. To compensate for this, the flake seizes other ions from outside sources, some of which become loosely attached to the crystal surface while others swarm about in the micelle. Such ions are generally cations (positive sign) and they may be either bases or hydrogen.

Base Exchange

Not all the bases have the same degree of affinity for the clay particle, in fact there is a definite order of preference. When a preferred ion is present in the surrounding water, it replaces an ion of a lower order in the micelle. Physicists have compiled this sequence: Calcium, Magnesium, Potassium, Hydrogen, Sodium, Lithium.

Calcium dominates and will replace any of the other bases below it in the list and that fact accounts for the decided changes that occur in sodium bentonite suspensions when a calcium-containing compound is added to the water.

The type of replaceable base originally dominant in the clay is probably responsible for the magnitude of its swelling and the amount of water which it will absorb. Sodium induces high solvation, swelling and suspendibility; when it is replaced by calcium the swelling of the bentonite is greatly reduced. Natural calcium bentonites such as occur in the South (for example, Panther Creek bentonite) are practically non-swelling.

Measuring Base Exchange

The exchangeable bases of clays are determined by a laboratory procedure of leaching and analysis, and the amounts being expressed in milli-equivalents per 100 grams of clay. Certain of the physical activities of the clay can be predicted from the results of such a test. Comparative figures of three bentonites and two other clays are shown in Table 1.

Effect of Electrolytes

Electrolytes are substances—they may be acids, bases or salts—which are dissociated or liberated in water to form charged particles or ions. The

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W. H. Herriott

Volclay Bentonite

To:

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TABLE 1. EXCHANGEABLE METALLIC BASES In Milli-equivalents per 100 grams

	BENTONITES			OTHER CLAYS	
	Volclay Wyoming	*Panther Creek Mississippi*	*Lovite Nevada*	*Ohio Plastic Fire Clay*	*Kentucky Ball Clay*
Calcium	22.0	64.7	51.5	5.2	7.1
Sodium	85.5	0.4	33.6	0.4	0.5
Potassium	5.0	2.8	1.1	0.5	0.4
Magnesium	1.0	1.0	19.1	1.3	3.8
Sum	89.2*	60.1*	78.1*	7.4	11.8

*Corrected for sulphates.

ions thus diffused are negatively or positively charged and they may carry one, two, three or more ionic charges (uni-valent, di-valent, tri-valent, etc.). Ionizing substances may act through simple contact with merely slightly moist bentonite, but they act more intensively in sols and for the purposes of this article we will consider only the sol or disperse system.

The influence of electrolytes on clay-water systems of ordinary clays has been the subject of a vast amount of research by noted soil chemists and colloid authorities and in the last few years similar work has been initiated with bentonite suspensions. Sodium bentonite is particularly susceptible because of its stronger electric charges; the greater surface area of its flakes; the sponge-like character of its lattice which permits the free ingress and egress of ions which may be present in the water; its suspendibility and mobility in water which gives more opportunities for collision with other floating ions.

Electrolytes change the character of bentonite suspensions in many respects; under some conditions they thicken it, under others they make it thinner, reducing the viscosity and increasing filterability. The results are determined by three principal factors; the kind of electrolyte, the concentration of bentonite to water and the concentration of electrolyte relative to bentonite.

Mono-valent ions are only mildly influential; di-valent ions much more effective and tri-valent ions tremendously more so, the relation being sometimes stated at 1-30-1000. An excess of either negative or positive ions depolarizes the bentonite particles so that they no longer repel each other and coalescence and floculation ensues. It is not scientifically established that depolarization is the only cause; "desolvation" or a change in the bound water of the micelle, may also be responsible and could occur through the substitution of ions having less water holding capacity. The size of the ion may also be an influence, hydrogen for example being very small and therefore numerically more hydrogen atoms can be packed into the channels between the flakes. Ions possessing thick water hulls, when attached to the outer surface of the particle, are held further away from it, from which various deductions can be made.

Clay water systems may contain both positively and negatively charged electrolytes and those with high and low valences and they may modify each other. The bentonite itself is an electrolyte and when complicated by other electrolytes in the water, the results are predictable only in a general way and are best ascertained by empirical experiments.

Except for a few general rules such as the dominance of either calcium or sodium, the chemical analysis of a bentonite sample does not permit exact evaluation of its properties of swelling, gelling and suspending even in distilled water. The data on this subject is constantly being accumulated and sifted; the broad path is fairly clear but it is crossed by devious trails which have not yet been mapped.

Volclay and Panther Creek bentonite are produced only by

AMERICAN COLLOID COMPANY, Merchandise Mart Plaza, Chicago 54

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